

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

**M. VIKRAM RAO**

Serial No.: **10/631,954**

Filed: **JULY 30, 2003**

Title: **"IMPROVED PARTICULATES AND  
METHODS OF UTILIZING THESE  
PARTICULATES IN SUBTERRANEAN  
APPLICATIONS"**

§  
§  
§  
§  
§  
§  
§  
§  
§

Group Art Unit: **1773**

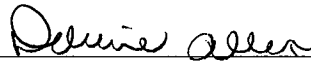
Examiner: **LE, HOA T.**

Atty. Docket No: **2003-IP-010829U1**

**CERTIFICATE OF FILING ELECTRONICALLY VIA EFS  
MPEP 503**

I HEREBY CERTIFY THAT I HAVE A REASONABLE BASIS FOR BELIEF  
THAT THIS CORRESPONDENCE IS BEING SUBMITTED TO THE UNITED  
STATES PATENT AND TRADEMARK OFFICE VIA EFS  
(ELECTRONICALLY) ON THE DATE INDICATED BELOW, AND IS  
ADDRESSED TO:

MAIL STOP APPEAL BRIEF – PATENTS  
HONORABLE COMMISSIONER FOR PATENTS  
P.O. BOX 1450  
ALEXANDRIA, VA 22313-1450



DEBBIE ALLEN

DATE OF SUBMISSION:  
ELECTRONIC FILING (EFS): JANUARY 10, 2007

**MAIL STOP APPEAL BRIEF – PATENTS  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450**

**APPELLANT'S BRIEF (37 C.F.R. § 41.37)**

This brief is submitted in support of Applicant's Notice of Appeal from the rejections in the Final Office Action dated May 12, 2006 (the "Final Office Action"), the Advisory Action dated August 10, 2006 (the "Advisory Action"), and the Notice of Panel Decision from Pre-Appeal Brief Review dated November 15, 2006.

Pursuant to the Notice of Panel Decision from Pre-Appeal Brief Review dated November 15, 2006, the shortened statutory period for filing this Appeal Brief was reset to one month from the mailing date of that Notice, and thus ended on December 15, 2006. This Appeal Brief is being submitted with a request for a one-month extension of time and the appropriate

fee, thus extending the period for filing to January 15, 2007. Therefore, this Appeal Brief is timely filed.

**I. IDENTIFICATION OF THE REAL PARTIES OF INTEREST**

The real party in interest is:

Halliburton Energy Services, Inc.  
10200 Bellaire Blvd.  
Houston, Texas 77072

by virtue of assignment by the inventor as duly recorded in the Assignment Branch of the U.S. Patent and Trademark Office.

**II. IDENTIFICATION OF RELATED APPEALS AND INTERFERENCES**

There are no related appeals or interferences, to Applicant's knowledge.

**III. STATUS OF THE CLAIMS**

The application as originally filed contained 59 claims. Claims 18-59 were previously withdrawn. Claims 1-17 are pending.

The Examiner has rejected claims 1-17 under 35 U.S.C. § 102(e) as being anticipated by U.S. Patent No. 6,913,643 to Dejaiffe ("*Dejaiffe*").<sup>1</sup> Applicant disagrees with these rejections.

Applicant herein appeals the rejections of claims 1-17 as improperly rejected. A listing of all appealed claims is provided in Appendix A in this Brief.

**IV. STATUS OF ANY AMENDMENT FILED SUBSEQUENT TO FINAL REJECTION**

Claim 10 was amended in Applicant's response to the Final Office Action to require that the particulates recited therein comprise a substantially spherical shape. The Examiner issued an Advisory Action indicating that this amendment would be entered for purposes of appeal. (See Advisory Action at ¶ 7.) Therefore, the listing of claims provided in Appendix A in this Brief reflects this amendment.

**V. SUMMARY OF THE CLAIMED SUBJECT MATTER**

Applicant's invention relates to improved particulates suitable for use in subterranean applications. More particularly, the present invention relates to reduced specific gravity particulates that comprise a substantially spherical shape.

---

<sup>1</sup> A copy of *Dejaiffe* is attached as Appendix E to this Brief.

Certain embodiments of Applicant's invention provide particulates comprising silica, an aluminum oxide in an amount of less than about 25%, and at least one void, wherein the particulates have a specific gravity of less than about 2.2, a particle size of 8 U.S. Mesh or smaller, and a substantially spherical shape (*See* claim 1.) In certain embodiments, the particulates may further comprise calcium oxides. (*See* claim 4.) In some embodiments, such particulates may have a particle size of 25 U.S. Mesh or smaller. (*See* claim 6.) In certain embodiments, the particulate may further comprise a vitrified outer layer. (*See* claim 8.)

Other embodiments of Applicant's invention provide particulates comprising at least about 30% silica, less than about 25% aluminum oxides, a plurality of internal voids, and a substantially spherical shape. (*See* claim 10.) In certain embodiments, the particulates may further comprise calcium oxides. (*See* claim 13.) In some embodiments, such particulates may have a particle size of 25 U.S. Mesh or smaller. (*See* claim 15.) In certain embodiments, the particulate may further comprise a vitrified outer layer. (*See* claim 17.)

## **VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL**

The Examiner has rejected claims 1-17 under 35 U.S.C. § 102(e) as being anticipated by U.S. Patent No. 6,913,643 to Dejaille ("*Dejaille*").<sup>2</sup> These rejections are improper.

## **VII. ARGUMENTS**

In the Final Office Action, the Examiner rejected claims 1-17 under 35 U.S.C. § 102(e) as being anticipated by *Dejaille*. These rejections are improper.

To form a basis for a § 102(e) rejection, a prior art reference must disclose, either expressly or inherently, each and every element as set forth in the claim. *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987); MANUAL OF PATENT EXAMINING PROCEDURE (hereinafter "MPEP") § 2131 (2006). In order to inherently disclose an element of a claim, "the extrinsic evidence 'must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill. Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient.'" *In re Robertson*, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999) (internal citations omitted); *see In re Rijckaert*, 9 F.3d 1531,

---

<sup>2</sup> A copy of *Dejaille* is attached as Appendix E to this Brief.

1534, 28 USPQ2d 1955, 1957 (Fed. Cir. 1993) (reversed rejection where inherency was based on what would result due to optimization of conditions, not what was necessarily present in the prior art); *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990) (reversed rejection based on inherent anticipation where the examiner did not provide sufficient evidence or technical reasoning to support the conclusion that required characteristic was present in the end product produced in the prior art, even where the prior art mentioned that characteristic with respect to the starting material). The rejections of claims 1-17 under § 102(e) should be reversed because (1) *Dejaiffe* does not disclose, either expressly or inherently, particulates that comprise a substantially spherical shape, as recited in independent claims 1 and 10, from which the remaining claims each depend, (2) *Dejaiffe* does not disclose particulates having a particle size of 8 U.S. Mesh or smaller, as recited in independent claim 1, and (3) *Dejaiffe* does not disclose particulates having a particle size of 25 U.S. Mesh or smaller, as recited in dependent claims 6 and 15.

**A. *Dejaiffe* cannot anticipate claims 1-17 because *Dejaiffe* fails to disclose the shapes of the aggregates discussed therein, and therefore, does not disclose aggregates having a substantially spherical shape as Applicant's claims require.**

**1. *Dejaiffe* specifies no shapes of the aggregates whatsoever, and therefore does not explicitly teach aggregates having a spherical shape.**

First, *Dejaiffe* does not disclose or even mention any specific shapes of the aggregates described therein. *Dejaiffe* merely discloses "lightweight aggregates" that may be large or small in size, and discloses that the size and shape of certain aggregates may be controlled by using a mold of a particular size and shape. (See *Dejaiffe* at col. 5, ll. 21-25). However, *Dejaiffe* makes no mention whatsoever of what these shapes might be, much less does it disclose that those aggregates may comprise a substantially spherical shape, as Applicant's claims require. Without any disclosure of the shape of the aggregates formed therein, *Dejaiffe* cannot explicitly anticipate Applicant's claimed invention. See *Richardson v. Suzuki Motor Co.*, 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989) ("The identical invention must be shown in as complete detail as is contained in the . . . claim.")

**2. *Dejaiffe* does not implicitly disclose spherical aggregates because the aggregates disclosed in *Dejaiffe* do not necessarily comprise a “substantially spherical shape.”**

As discussed above, *Dejaiffe* does not expressly disclose particulates having a substantially spherical shape. The Examiner has not disputed this. After failing to discuss this element at all in the Final Office Action, the Examiner asserted for the first time in the Advisory Action that processes disclosed in *Dejaiffe* will “inherently produce particulates that are substantially spherical.” (Advisory Action at ¶ 1.) This is incorrect.

The processes disclosed in *Dejaiffe* do not necessarily produce particulates having a substantially spherical shape. *Dejaiffe* discusses processes of generating certain aggregates generically, and discloses ranges of possible amounts of starting materials that could be used to produce the aggregates (*see, e.g., Dejaiffe* at col. 4, ll. 5-10), which may include an infinite number of specific amounts of those materials. *Dejaiffe* gives no indication to one skilled in the art that aggregates produced using any of the processes disclosed therein necessarily will have a substantially spherical shape. Nor does the Examiner cite to any reference or source of extrinsic evidence showing that the processes disclosed in *Dejaiffe* necessarily produce particulates having a substantially spherical shape. Indeed, the processes of sintering and pelletization may produce aggregates of all different shapes, which may or may not be substantially spherical. *See, e.g.,* RANDALL M. GERMAN, SINTERING THEORY AND PRACTICE 260 (John Wiley & Sons, Inc. 1996) (discusses formation of spherical and angular grain shapes in sintering); U.S. Patent No. 3,125,794 (issued March 24, 1964) at col. 3, ll. 12-17 (pellets may be molded into various different sizes or shapes); *id.* at col. 4, ll. 27-28 (“It is further apparent that the present invention is applicable to the formation of non-spherical pellets.”).<sup>3</sup> Thus, *Dejaiffe*’s disclosure of sintering and pelletization processes, without more, does not inherently disclose a process that necessarily produces particles having substantially spherical shape. *Ex parte Levy*, 17 USPQ2d at 1464 (examiner must provide sufficient evidence or technical reasoning to support the conclusion that required characteristic is present in the end product produced in the prior art). The fact that these processes may produce particulates of a substantially spherical shape does not establish that such particulates are necessarily produced. *Robertson*, 169 F.3d at 745, 49 USPQ2d at 1950-51; *see In re Rijckaert*, 9 F.3d at 1534, 28 USPQ2d at 1957 (characteristic is

---

<sup>3</sup> Copies of these references are provided in Appendix B. Applicant did not present this evidence prior to the filing of this Appeal Brief since the Examiner only asserted that *Dejaiffe* inherently discloses particulates having a substantially spherical shape for the first time in the Advisory Action issued after the Final Office Action.

not inherent where that characteristic requires optimization of conditions beyond what is disclosed in the prior art).

Moreover, there is no teaching in *Dejaiffe* of which processes would produce particulates having a substantially spherical shape. Even if particulates of that shape could be formed using these processes disclosed in *Dejaiffe*, one of ordinary skill in the art would not recognize it as such from the teachings contained in the reference. Thus, *Dejaiffe* does not inherently disclose substantially spherical particulates. *See id.* (extrinsic evidence “must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill”).

Thus, the Examiner has not shown that the processes described in *Dejaiffe* will “necessarily” produce particulates having a substantially spherical shape, as required in Applicant’s claims, or that it would be so recognized by persons of skill in the art. Accordingly, *Dejaiffe* cannot anticipate Applicant’s claims.

**3. The Examiner improperly relies on Applicant’s specification to erroneously conclude that the aggregates in *Dejaiffe* inherently have a substantially spherical shape.**

Lacking any proper evidence to support the supposition that the processes disclosed in *Dejaiffe* necessarily produce particulates having a substantially spherical shape, the Examiner improperly relies on a portion of Applicant’s description of the invention in the specification in an attempt to provide an explanation for this hypothesis:

This inherence fact is actually acknowledged by Applicant. At page 7, paragraph 25 of the instant specification, it’s stated: “When such combustion products are pelletized and sintered, they produce particulates that are substantially spherical and that exhibit specific gravities of below about 2.2.” Therefore, not only aggregates of *Dejaiffe* possess spherical shape, they also exhibit specific gravities of below 2.2 as claimed.

(Advisory Action at ¶ 1.)

However, the basis in fact and/or technical reasoning necessary to supply the teaching of a claim element inherent in the prior art must come from the extrinsic evidence available to a person of skill in the art. *See Robertson*, 169 F.3d at 745, 49 USPQ2d at 1950-51; *Continental Can Co. USA v. Monsanto Co.*, 948 F.2d 1264, 1268, 20 USPQ2d 1746, 1749 (Fed. Cir. 1991) (“To serve as an anticipation when the reference is silent about the asserted inherent characteristic, such gap in the reference may be filled with recourse to extrinsic evidence. Such

evidence must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill.” (emphasis added)); MPEP at § 2112. Applicant’s descriptions of the shape of the particulates generated according to their own invention cannot inform or support the interpretation of *Dejaiffe* on which the Examiner relies to anticipate Applicant’s claimed invention.

The specific sentence to which the Examiner refers is found in the section of Applicant’s disclosure entitled “Description of Preferred Embodiments,” (*i.e.*, the description of Applicant’s invention) rather than the Background section or a section characterizing the prior art. The Description of Preferred Embodiments section describes, among other things, the composition of certain combustion products, and then, with reference to those specific combustion products, states that, “[w]hen such combustion products are pelletized and sintered, they produce particulates that are substantially spherical and that exhibit specific gravities of below about 2.2.” (*See* Specification at ¶ [025].)<sup>4</sup> This statement does not pertain to or bear on the prior art of Applicant’s invention. Nor does this statement imply in any way that all processes of pelletizing and sintering combustion products necessarily generate particulates with a substantially spherical shape. Indeed, as discussed in Section VII.A.2. above, these processes may yield particulates of any number of varied shapes. Rather, this sentence describes the manner in which a person of skill should make or use Applicant’s claimed invention in a manner not described, either explicitly or inherently, in *Dejaiffe*. Applicant’s disclosure of the claimed invention instructs and enables the production of particulates having a substantially spherical shape, but this enabling disclosure does not indicate or imply that the particulates disclosed in *Dejaiffe* or any other prior art reference necessarily will have this shape. Thus, the Examiner’s attempt to extrapolate from Applicant’s teachings regarding their particular invention to conclude that *Dejaiffe* inherently teaches the features of that invention is improper.

Thus, since *Dejaiffe* does not disclose this element of claims 1 and 10, *Dejaiffe* does not anticipate those claims. Moreover, claims 2-9 and 11-17 each depend, either directly or indirectly, from claim 1 or 10, and thus incorporate the limitations of claim 1 or 10 that *Dejaiffe* does not disclose. Therefore, claims 1-17 are allowable over *Dejaiffe*, and Applicant respectfully requests the reversal of the rejections against these claims.

---

<sup>4</sup> A copy of the specification as filed is provided in Appendix D in this Brief.

**B. *Dejaiffe* cannot anticipate claims 1-9 because *Dejaiffe* fails to specify any particular size of the aggregates disclosed therein, and therefore does not disclose a particle size of 8 U.S. Mesh or smaller, as required in independent claim 1.**

The rejections of claims 1-9 under 35 U.S.C. § 102(e) are further improper because, in addition to the reasons discussed above with respect to independent claims 1 and 17 in Section VII.A. above, *Dejaiffe* does not disclose particulates having a particle size of 8 U.S. Mesh or smaller, as required in independent claim 1. *Dejaiffe* specifies no measured size or range of measured sizes that the aggregates discussed therein may have. The only discussion in *Dejaiffe* of the size of the aggregates vaguely states that “[p]referably, the lightweight aggregate of the present invention can be formed in large and small sizes.” (*Dejaiffe* at col. 4, l. 66 – col. 5, l. 1.) However, neither this statement nor the balance of *Dejaiffe* offers any guidance or indication as to the actual size of these “large” or “small” aggregates. Thus, *Dejaiffe*’s broad, qualitative characterization of the size of the aggregates as being “large” or “small” would not instruct a person of ordinary skill in the art to produce particulates to have sizes specifically in the range of 8 U.S. Mesh or smaller.

Thus, since *Dejaiffe* does not disclose this element of claim 1, *Dejaiffe* does not anticipate claim 1. Moreover, claims 2-9 each depend, either directly or indirectly, from claim 1, and thus incorporate the limitations of claim 1 that *Dejaiffe* does not disclose. Therefore, claims 1-9 are allowable over *Dejaiffe*, and Applicant respectfully requests the reversal of the rejections against these claims.

**C. *Dejaiffe* cannot anticipate dependent claims 6 and 15 because *Dejaiffe* fails to specify any particular size of the aggregates disclosed therein, and therefore does not disclose particle size of 25 U.S. Mesh or smaller, as claims 6 and 15 recite.**

The rejections of dependent claims 6 and 15 under 35 U.S.C. § 102(e) are further improper because, in addition to the reasons discussed above with respect to independent claims 1 and 17 in Section VII.A. above, *Dejaiffe* does not disclose particulates having a particle size of 25 U.S. Mesh or smaller, as required in these claims. As discussed in Section VII.B. above, *Dejaiffe* specifies no measured size or range of measured sizes that the aggregates discussed therein may have, and the vague discussion in *Dejaiffe* that the aggregates disclosed therein “can be formed in large and small sizes” would not instruct a person of ordinary skill in the art to produce particulates to have sizes specifically in the range of 25 U.S. Mesh or smaller.



Thus, since *Dejaiffe* does not disclose this element of claims 6 and 15, *Dejaiffe* does not anticipate those claims. Therefore, dependent claims 6 and 15 are allowable over *Dejaiffe*, and Applicant respectfully requests the reversal of the rejections against these claims.

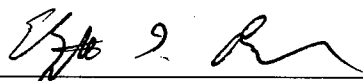
**VIII. SUMMARY AND PETITION FOR A ONE-MONTH EXTENSION OF TIME TO FILE THIS BRIEF**

In light of the foregoing, Applicant respectfully requests that the final rejection of the pending claims should be reversed and the application be remanded for allowance of the pending claims, or, alternatively, remand the application for further examination if appropriate references can be found by the Examiner.

Applicant hereby petitions under the provisions of 37 C.F.R. § 1.136(a) for a one-month extension of time to file this Brief, up to and including January 15, 2007.

The Commissioner is hereby authorized to debit Baker Botts L.L.P.'s Deposit Account No. 02-0383, Order Number 063718.0285, in the amount of \$620.00 for (1) the fee of \$120.00 under 37 C.F.R. § 1.17(a)(1) for the One-Month Petition for Extension of Time to File this Brief, and (2) the fee of \$500.00 under 37 C.F.R. § 41.20(b)(2) for filing an appeal brief. Should the Commissioner deem that any additional fees are due, including any fees for extensions of time, the Commissioner is authorized to debit Baker Botts L.L.P.'s Deposit Account No. 02-0383, Order Number 063718.0285.

Respectfully submitted,

  
\_\_\_\_\_  
Elizabeth L. Durham  
Registration No. 59,509  
BAKER BOTTS L.L.P.  
One Shell Plaza  
910 Louisiana  
Houston, TX 77002  
Telephone: 713.229.2104  
Facsimile: 713.229.7704  
Email: liz.durham@bakerbotts.com

Date: January 10, 2007

**APPENDIX A: CLAIMS INVOLVED IN APPEAL**

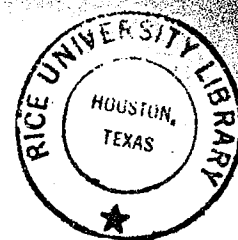
1. (Previously Presented) Particulates comprising silica, an aluminum oxide in an amount of less than about 25%, and at least one void, the particulates having a specific gravity of less than about 2.2, a particle size of 8 U.S. Mesh or smaller, and a substantially spherical shape.
2. (Original) The particulates of claim 1 comprising from about 30 percent to about 70 percent by weight silica.
3. (Previously Presented) The particulates of claim 1 comprising from about 0.1 percent to about 25 percent by weight aluminum oxide.
4. (Original) The particulates of claim 1 further comprising calcium oxides.
5. (Previously Presented) The particulates of claim 1 wherein the silica and aluminum oxide comprise combustion products of carbonaceous materials.
6. (Original) The particulates of claim 1 comprising a particle size of 25 U.S. mesh or smaller.
7. (Original) The particulates of claim 1 wherein the particulate is capable of withstanding a closure stress of at least about 2,500 psi.
8. (Original) The particulates of claim 1 comprising a vitrified outer layer.
9. (Original) The particulates of claim 1 wherein at least one void communicates between an interior of the particulate, and a surface of the particulate and environment surrounding the particulate.
10. (Previously Presented) Particulates comprising at least about 30% silica, less than about 25% aluminum oxides, a plurality of internal voids, and a substantially spherical shape.
11. (Original) The particulates of claim 10 comprising at least about 40 percent by weight silica.
12. (Original) The particulates of claim 10 comprising less than about 20% by weight aluminum oxides.
13. (Original) The particulates of claim 10 further comprising calcium oxides.
14. (Original) The particulates of claim 10 wherein the silica and aluminum oxides comprise combustion products of carbonaceous materials.
15. (Original) The particulates of claim 10 comprising a particle size of 25 U.S. mesh or smaller.

16. (Original) The particulates of claim 10 wherein the particulate is capable of withstanding a closure stress of at least about 2,500 psi.
17. (Original) The particulates of claim 10 comprising a vitrified outer layer.

**APPENDIX B: EVIDENCE**

Contents:

1. RANDALL M. GERMAN, SINTERING THEORY AND PRACTICE 258-260 (John Wiley & Sons, Inc. 1996).
2. U.S. Patent No. 3,125,794 to Carl E. Reynolds (issued March 24, 1964).



---

# SINTERING THEORY AND PRACTICE

---

Randall M. German

The Pennsylvania State University  
University Park, Pennsylvania

TS  
245  
.G48  
1996



A WILEY-INTERSCIENCE PUBLICATION

**JOHN WILEY & SONS, INC.**

New York / Chichester / Brisbane / Toronto / Singapore

Q 95020223

This text is printed on acid-free paper.

Copyright © 1996 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012.

*Library of Congress Cataloging in Publication Data:*

German, Randall M., 1946-

Sintering theory and practice / by Randall M. German.

p. cm.

Includes bibliographical references and index.

ISBN 0-471-05786-X (alk. paper)

1. Sintering. I. Title.

TS245.G48 1996

671.3'73--dc20

95-20223

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

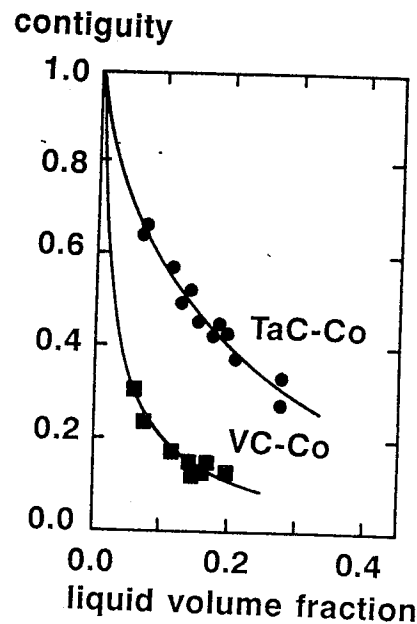


Figure 6.31. Data from Warren and Waldron [30] showing the solid contiguity versus the liquid content for two cemented carbide liquid-phase materials sintered at 1450°C.

A change in the solid-solid grain boundary or the solid-liquid surface energy ( $\gamma_{ss}$  and  $\gamma_{sl}$ ) results in a change in the dihedral angle and contiguity. Since the surface energy varies during the initial portion of liquid-phase sintering, a corresponding contiguity variation also occurs. Figure 6.33 plots this behavior for a W-Ni alloy sintered at 1550°C [32]. The change in contiguity relates to the surface energy and dihedral angle changes shown earlier in Figure 6.24. Usually, a constant value is reached at long sintering times.

### Grain Shape

The shape of a solid grain depends on several factors but is affected most by the dihedral angle, liquid content, and surface energy anisotropy. Nearly flat contacts form between neighboring grains. These contacts allow the grains to change shape to attain better packing. For dihedral angles over 60° and small volume fractions of liquid, the liquid structure is dispersed along grain edges and is not continuous. At large dihedral angles, typically over 90°, the microstructure is unstable for all quantities of liquid. Consequently, the liquid exudes from the compact, as evident in Figure 6.34. Practical interest is in systems with dihedral angles below 60°.

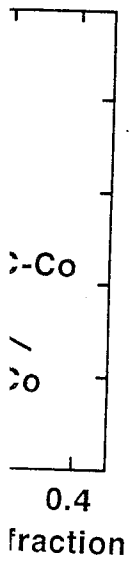


Figure 6.31. Plot of the solid-liquid surface dihedral angle versus the liquid fraction for a system sintered at 1450°C.

or the solid-liquid surface dihedral angle and contiguity. A portion of liquid-phase sintering occurs. Figure 6.33 plots this [32]. The change in contiguity angle changes shown earlier in [31] at long sintering times.

Factors but is affected most by energy anisotropy. Nearly flat grain contacts allow the grains to sinter at large angles over 60° and small angles over 90°, the microstructure is dispersed along grain edges. Consequently, the liquid exudes of interest is in systems

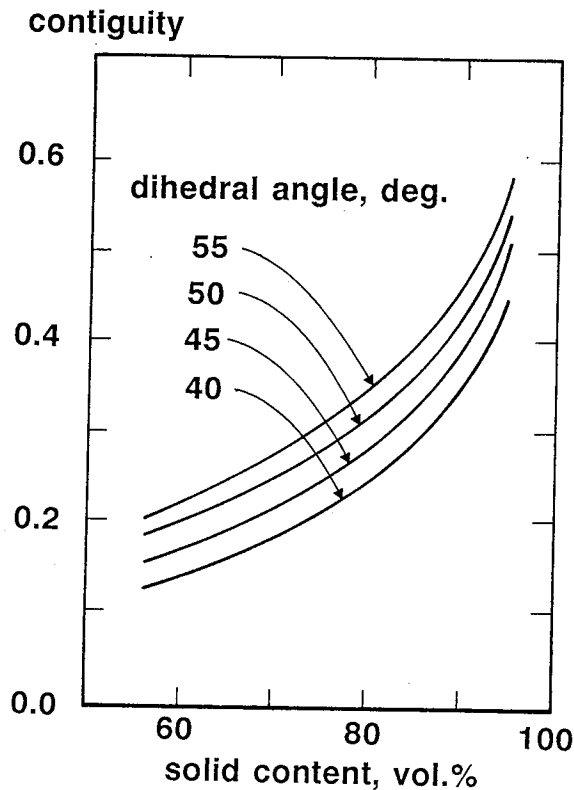


Figure 6.32. Model predictions of the contiguity dependence on the solid content for various dihedral angles in systems with standard grain size distributions and rounded grains [31].

Beere [33] and Wray [34] calculated the equilibrium grain-liquid shape under various conditions assuming zero porosity and a solid grain packing coordination of 14. Examples of six equilibrium liquid structures are given in Figure 6.35. These structures correspond to the six regions on the dihedral angle-volume fraction liquid map. A dihedral angle below about 70° leads to a concave liquid. With a sufficient amount of liquid, the structure is connected along the grain edges and is connected for all dihedral angles below 60°, independent of the amount of liquid. Alternatively, for low volume fractions of liquid and large dihedral angles, a discrete disconnected liquid microstructure is expected. An example of the grain-liquid shape is sketched in Figure 6.36, where the liquid (unshaded region) forms a continuous network along the three grain junctions. Only a portion of the liquid network is shown on this tetrakaidecahedron grain. Figure 6.37 is a scanning electron micrograph of such a network after chemical dissolution of the grain structure. The interlaced liquid (matrix) structure is evident in this micrograph. In contrast, Figure 6.38



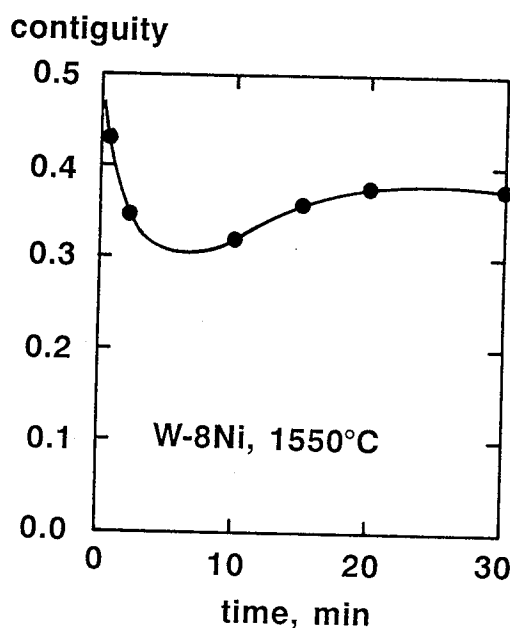


Figure 6.33. Contiguity versus sintering time for a W-8Ni compact sintered at 1550°C, showing variations due to surface energy changes during the initial solid-liquid reaction [32].

shows the shape of ZnO grains after dissolution of the liquid phase, with evidence of nonspherical shapes. The flat, circular faces on the grains indicate points of contact. At a low solid contents the grains are often rounded, approaching a spherical shape. However, a high solids content causes the grains to flatten along neighbor faces because of grain shape accommodation. Usually, the particle shape before liquid-phase sintering has no significant influence on the final grain shape.

As liquid-phase sintering progresses, the large grains grow at the expense of the smaller grains. Dissolution makes the smaller grains spherical. However, growing grains tend toward shapes dictated by either grain shape accommodation or anisotropic surface energies. Low-energy crystallographic orientations are favored, leading to faceting of the grains. Further, in systems where the surface energy varies with crystallographic orientation by more than approximately 15%, angular grain shapes are expected. Warren [35] provides an example calculation of grain shape assuming that the surface energy of the (100) plane in a cubic crystal deviated from a mean value for the crystal. Figure 6.39 gives the resulting grain shape as a function the solid-liquid surface energy deviation from the mean. Such an anisotropic surface energy effect is prevalent in the cemented carbides, as illustrated in Figure 6.40. This micrograph is from a random section through the sintered structure. The prismatic grain shape is dictated by the a nisotropic surface energy. Figure 6.41 is a

Figure 1  
melt is 1  
The con

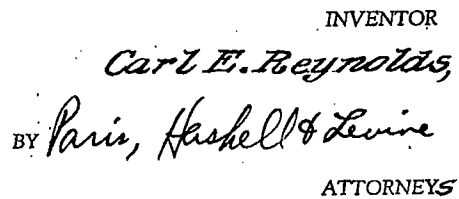
three-c  
shape  
respect  
evident

HEATI

The ini  
events 1  
is an im  
initial r  
lead to  
the con  
penetra  
formed  
rearran

**3,125,794**

Filed Oct. 3, 1962



ATTORNEYS

1

3,125,794

## MANUFACTURE OF PELLETS FROM A CAST STRIP

Carl E. Reynolds, St. Petersburg, Fla., assignor to  
Florida Fishing Tackle Mfg. Co., Inc., a corporation of  
Florida

Filed Oct. 3, 1962, Ser. No. 228,173  
3 Claims. (Cl. 29—1.22)

The present invention relates to the production of shot or pellets, and particularly, although not necessarily, to spherical pellets. Although it is contemplated that the present invention will find its greatest utility in the manufacture of lead shot, it is not limited to this material, and other metals and materials, such as suitable plastics and the like, can be utilized in the formation of pellets by the teachings of the present invention.

In accordance with the present invention, the pellets or shot are formed from a ribbon of the selected material. The ribbon may be preformed, or it may be continuously cast and formed as an integral step in the procedures of the present invention. In either event, the ribbon is fed through the nip of a pair of molding die rolls whose surfaces are formed with matching cavities which may be hemispherically or otherwise shaped, as desired. The ribbon is compressed between these rolls with sufficient pressure to cause the material of the ribbon to flow into the roll surface cavities, thereby forming sets of paired protuberances shaped in accordance with the roll cavities, with one set of protuberances projecting from one surface of the ribbon, and the other set of protuberances projecting from the opposite surface of the ribbon. All the protuberances remain united by means of a residual thin web of the original ribbon. This web is then passed through the nip of a pair of expressing rolls, where the paired pellet-like protuberances are pushed or pressed out of the retaining web as pellets or shot. In the case of spherical pellets, if desired the pellets may be worked into true spheres and the flashings and other irregularities removed by passing the pellets between the surfaces of a pair of oppositely rotating discs.

It is accordingly one object of the present invention to provide for the manufacture of pellets or shot.

Another object of the present invention is to provide for the continuous production of pellets by molding the pellets from a ribbon.

Another object of the present invention is to provide for the continuous production of pellets by continuously casting a ribbon of material, and molding the pellets from the ribbon.

Still another object of the present invention is to provide for the continuous casting of a ribbon of material.

Other objects and advantages of the present invention will become apparent to those skilled in the art from a consideration of the following detailed description of one exemplary embodiment thereof, had in conjunction with accompanying drawings, in which like reference characters refer to like or corresponding parts, and wherein:

FIG. 1 is a schematic diagram illustrating an apparatus for practicing the present invention; and

FIG. 2 is an enlarged sectional view taken along the line 2—2 of FIG. 1;

2

FIG. 3 is an enlarged sectional view taken along the line 3—3 of FIG. 1; and

FIG. 4 is an enlarged and fragmentary detailed cross-sectional showing of the ribbon casting apparatus, taken along the line 4—4 of FIG. 1.

Referring to FIG. 1, the material of which the pellets or shot are to be made, may be lead, and in that case a supply of molten lead is provided in a melting pot 10. The molten lead is fed from the pot 10 to the continuous ribbon casting apparatus 20. The lead ribbon 13 thus formed is drawn from the casting apparatus by compressing rolls 31 and 32 at sizing station 30 and there pressed to a desired thickness. The uniformly sized ribbon of lead is then fed into the nip of a pair of molding rolls 41 and 42, at the molding station 40, where the shot or pellets are molded as paired protuberances (shown as hemispherical) still united by a residual web of lead. At 50 the balls or pellets are pressed out of the web, collected between the oppositely rotating plates 62 and 63 at the spherical truing station 60, and thence fed to a collecting hopper 64. Meanwhile the residual web of lead issuing from the pellet expressing station 50 is collected by the scrap take up rolls 70.

Considering the apparatus of FIG. 1 in greater detail, reference is first had to the continuous ribbon casting apparatus 20, which is also partially shown in greater detail in FIG. 4. Casting apparatus 20 comprises a rotating wheel 21 having two peripheral circumferential flanges 22 and 23 which are axially spaced from each other, defining therebetween a continuous peripheral channel 24. A stationary shoe 25 is positioned in sliding engagement with the rim flanges 22 and 23 to define therewith and with channel 24 a confined mold cavity 29 of desired dimensions. The shoe 25 is hollow and is water cooled internally by the flow of cooling water into the shoe at 26 and out at 27. The top of the shoe is funneled at 28 to direct the flow of molten lead into the top of the casting cavity 29.

Thus molten lead is caused to flow from pot 10 under control of valve 11 through pipe 12 into the funnel 28 of shoe 25. This molten lead is directed into the mold cavity 29, and as wheel 21 rotates, the molten lead in cavity 29 is chilled and solidified by the water cooling of shoe 25, and issues at the bottom of the mold cavity as a solidified ribbon of lead 13. So long as the wheel 21 is rotated at the proper speed to permit solidification of the lead in the mold cavity 29, and the feed of molten lead is regulated therewith to maintain the mold cavity 29 filled with lead, a continuous ribbon of lead can be stripped from channel 24 at the bottom of wheel 21.

Molten lead can be maintained in proper supply in funnel 28, by means of valve 11, which may be automatically controlled. As shown in FIG. 1, this automatic control may be effected by an air piston motor 14 for operating the valve 11, and an electric solenoid valve 15 for controlling the feed of compressed air to, and exhaust of the piston motor 14, as will be fully understood by those skilled in the art. Conveniently, operation of the solenoid can be controlled by an electric circuit completed through the pool of lead in funnel 28. Thus, when the level of lead in funnel 28 is high enough to reach wire 16, the solenoid circuit is completed through the lead to energize the solenoid 15, and thereby shut valve 11. When the level of lead in funnel 28 falls below the level

at which the end of wire 16 is positioned, the circuit of solenoid 15 is opened, thereby deenergizing the solenoid to effect an opening of valve 11, as might be effected by a spring return operating on the piston of air motor 14.

The continuous lead ribbon thus issuing from casting station 20 is fed into the nip of two steel sizing rolls 31 and 32. The spacing between these rolls may be adjusted to obtain a desired uniform thickness of ribbon 13 issuing therefrom and feeding to pellet molding rolls 41 and 42.

Rolls 41 and 42 are identical. They comprise central cores 43 and 44, and peripheral molding sleeves 45 and 46. Each of the molding sleeves is formed with a regular pattern of hemispherical (or other desired shape) cavities 47 which mold the pellets. Sleeves 45 and 46 are removable in order to permit sleeves having different sized or shaped cavities 47 to be installed, for the molding of different sizes or shapes of pellets. Sleeve 45 is keyed at 48 to its roll core 43, and sleeve 46 is keyed at 49 to its roll core 44. These keys 48 and 49 function to locate the two sleeves 45 and 46 in precise relative angular relation to their cores and to each other in order that at the nip of the two rolls 41 and 42 a set of cavities 47 in sleeve 46 is precisely opposed to a corresponding set of cavities 47 in sleeve 45.

Thus, with rolls 41 and 42 set closer together than sizing rolls 31 and 32, as the ribbon 13 passes between the molding rolls 41 and 42, the compression of the ribbon by these rolls causes the lead to flow into the cavities 47 of each roll. Therefore, as ribbon 13 issues from the molding rolls it has a set of protruding hemispheres 17 formed on the upper surface, and a corresponding set of protruding hemispheres formed on the bottom surface, all joined together by a thin web of lead 18. In view of the registry of the two sets of cavities 47, each hemisphere molded on the upper surface of web 18 is paired with a similar hemisphere molded on the under side of web 18, with these two hemispheres located exactly opposite one another, and together forming a spherical pellet.

Ribbon 13, thus molded into protruding hemispheres connected by thin web 18, is passed to the pellet expressing station 50, where the protuberances 17 and their mating protuberances on the opposite side of web 13 are pressed out of the web to form the pellets 51. Pellet expressing station 50 comprises two rolls 52 and 53, between which the ribbon 13 is fed. Roll 52 comprises a steel backing core 54 having a covering blanket of rubber 55 vulcanized to the surface thereof. Roll 53 is formed with a number of perforations 56 arranged in a pattern corresponding in size, shape, and orientation to the cavities 47 on rolls 41 and 42. Roll 53 is made interchangeable with other perforated rolls to correspond with the particular sleeves 45 and 46 selected for rolls 41 and 42.

As the web 18 issuing from the molding station 40 is fed into the nip of rolls 52 and 53, the protuberances or hemispheres projecting from the lower surface of web 18 enter the perforations 56, while roll 52 applies a cushioned pressure to the upper surface protuberances 17. As a result, the paired protuberances or hemispheres are pressed out of the web 18, without serious deformation, as pellets 51, and as they fall from the web they are collected in funnel 61 of the truing station 60. Meanwhile the residual web 18 is fed to the scrap take-up rolls 70 and collected for reuse in the lead melting pot 10.

The truing station 60 is applicable particularly to the formation of truly spherical pellets. It comprises a pair of juxtaposed oppositely rotating disks 62 and 63 which are spaced apart axially by the exact diameter desired for pellets 51. The spacing between disks 62 and 63 is made adjustable to accommodate for different sized pellets formed by the selected molding sleeves 45 and 46 chosen for rolls 41 and 42. As the pellets 51 fall from the web 18, they are collected by funnel 61 and there introduced into the space between disks 62 and 63 about at the center thereof. As pellets 51 enter between the disks they are rotated or rolled over and over as they work

their way toward the periphery of the truing disks. During this rolling process, any flashings on the pellets 51 are removed, and they are formed into substantially true spheres. The spherical pellets issuing from the periphery of disks 62 and 63 are collected in a hopper 64.

It is apparent that wheel 20, rolls 31 and 32, rolls 41 and 42, rolls 52 and 53, and rolls 70 are all driven in timed relation, preferably by a single gear train or gear-chain arrangement, operated by one motor, in order that all operations be carried out in synchronism and the rate of feed of ribbon 13 be controlled at all stages to prevent an excess accumulation or stretching of the ribbon between stations. It is also apparent that a structural base for the apparatus is provided, as well as rotation axles for the rolls and mounting structure for all the parts. However, since all these structural elements are conventional, are not per se part of the present invention, and would be design features readily apparent to those skilled in the art, they are not illustrated in the present drawings, as they would serve only to confuse rather than to clarify the present invention.

Although herein specifically described in relation to the manufacture of spherical lead pellets or shot, it is apparent that the present method and apparatus and parts thereof are applicable to the manufacture of pellets from other malleable materials, such as other metals and suitable plastics. It is further apparent that the invention is applicable to the formation of non-spherical pellets. Accordingly, since numerous variations, modifications and changes in the herein described specific embodiment will be apparent to those skilled in the art, it is not intended that the present invention be construed as restricted to this embodiment; but such variations, changes and modifications as are embraced by the spirit and scope of the appended claims are contemplated as within the purview of the present invention.

What is claimed is:

1. An apparatus for forming pellets, comprising: a supply container; means for casting a flat ribbon including a rotatably mounted wheel having a peripheral circumferential rectangular channel, a stationary shoe fitted over a portion of the circumferential periphery of said wheel in sliding engagement therewith to form a casting cavity between said shoe and said channel, and means for cooling said shoe; means for conducting a flow of molten material from said supply container to said cavity, and means for controlling the rate of flow of said molten material; said molten material being solidified in said cavity by said cooling means, and rotation of said wheel causing the issuance of a continuous flat ribbon of said material from said cavity; means for sizing said ribbon into a desired uniform thickness, including a pair of pressure rolls between which said ribbon is passed; means for molding pellets from said ribbon, including a pair of compression molding rolls between which the sized ribbon is passed, said molding rolls having cavities formed over the periphery thereof, whereby said ribbon is compressed therebetween causing the ribbon material to flow into said cavities to produce a plurality of molded protuberances projecting from the surface of said ribbon; and means for pressing said molded protuberances from said ribbon, including a pair of pressure rolls between which the molded ribbon is passed, one of said pressure rolls having a plurality of perforations of a size to correspond approximately with said protuberances, the other of said pressure rolls having a continuous cushioned surface, whereby said molded protuberances are pushed by said other pressure roll from said ribbon and through the perforations in said one pressure roll to form pellets from said ribbon.

2. An apparatus for forming pellets as set forth in claim 1, and further including means for truing said pellets into substantially spherical shape and removing flashings therefrom, comprising a pair of juxtaposed oppositely rotating disks axially spaced apart a distance equal to

5

the diameter desired for said pellets, and means for introducing said pellets pressed from said ribbon between said disks near the centers thereof, whereby said pellets are rotated over and over between said disks and issue from the periphery of said disks as substantially true spheres.

3. An apparatus for forming pellets from a moldable material in ribbon form comprising, a pair of compression molding rolls between which the ribbon is passed, said molding rolls having cavities formed over the periphery thereof, whereby said ribbon is compressed therebetween causing the ribbon material to flow into said cavities to produce a plurality of molded pellet-like protuberances in said ribbon, and a pair of pressure rolls between which the molded ribbon is passed, one of said pressure rolls having a plurality of perforations of a size to correspond approximately with said pellet-like protuberances, the

5

10

15

6

other of said pressure rolls having a continuous cushioned surface, whereby said pellet-like protuberances are pressed out of said ribbon by said other pressure roll and through said perforations to form pellets.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

358,984	Quackenbush	Mar. 8, 1887
767,831	Pearson et al.	Aug. 16, 1904
1,674,112	Hering	June 19, 1928
2,206,930	Webster	July 9, 1940
2,327,894	Hodgson	Aug. 24, 1943
2,682,691	Harter	July 6, 1954
2,782,487	Properzi	Feb. 26, 1957
2,931,082	Brennan	Apr. 5, 1960

**APPENDIX C: RELATED PROCEEDINGS**

None

**APPENDIX D: SPECIFICATION AS FILED**

**IMPROVED PARTICULATES AND METHODS OF UTILIZING THESE  
PARTICULATES IN SUBTERRANEAN APPLICATIONS**

**1. Field of the Invention.**

[001] The present invention relates to improved particulates and methods of using such particulates in subterranean applications. More particularly, the present invention relates to reduced specific gravity particulates and their use in subterranean applications such as production enhancement and completion.

**2. Description of the Prior Art.**

[002] Servicing fluids comprising particulates are used in a variety of operations and treatments performed in oil and gas wells. Such operations and treatments include, but are not limited to, production stimulation operations such as fracturing and well completion operations such as gravel packing.

[003] An example of a production stimulation operation using a servicing fluid having particles suspended therein is hydraulic fracturing. That is, a type of servicing fluid, referred to in the art as a fracturing fluid, is pumped through a well bore into a subterranean zone to be stimulated at a rate and pressure such that fractures are formed and extended into the subterranean zone. The fracture or fractures may be horizontal or vertical, with the latter usually predominating, and with the tendency toward vertical fractures increasing with the depth of the formation being fractured. The fracturing fluid is generally a gel, emulsion, or foam that may comprise a particulate material often referred to as proppant. The proppant is deposited in the fracture and functions, *inter alia*, to hold the fracture open while maintaining conductive channels through which such produced fluids can flow upon completion of the fracturing treatment and release of the attendant hydraulic pressure.

[004] An example of a well completion operation using a treating fluid containing particulates is gravel packing. Gravel packing treatments are used, *inter alia*, to reduce the migration of unconsolidated formation particulates into the wellbore. In gravel packing operations, particles referred to in the art as gravel are carried to a well bore in a subterranean producing zone by a hydrocarbon or water carrier fluid. That is, the particulates are suspended in



a carrier fluid, which may be viscosified, and the carrier fluid is pumped into a well bore in which the gravel pack is to be placed. As the particulates are placed in the zone, the carrier fluid leaks off into the subterranean zone and/or is returned to the surface. The resultant gravel pack acts as a filter to separate formation solids from produced fluids while permitting the produced fluids to flow into and through the well bore. While screenless gravel packing operations are becoming more common, traditional gravel pack operations involve placing a gravel pack screen in the well bore and packing the surrounding annulus between the screen and the well bore with gravel sized to prevent the passage of formation particulates through the pack with produced fluids. The gravel pack screen is generally a filter assembly used to support and retain the gravel placed during the gravel pack operation. A wide range of sizes and screen configurations are available to suit the characteristics of a well bore, the production fluid, and any particulates in the subterranean formation. When installing the gravel pack, the gravel is carried to the formation in the form of a slurry by mixing the gravel with a viscosified carrier fluid. Once the gravel is placed in the wellbore, the viscosity of the carrier fluid is reduced and it is returned to the surface. Such gravel packs are used to stabilize the formation while causing minimal impairment to well productivity. The gravel, *inter alia*, acts to prevent the particulates from occluding the screen or migrating with the produced fluids, and the screen, *inter alia*, acts to prevent the gravel from entering the well bore.

[005] In some situations the processes of hydraulic fracturing and gravel packing are combined into a single treatment to provide a stimulated production and an annular gravel pack to prevent formation sand production. Such treatments are often referred to as "frac pack" operations. In some cases the treatments are completed with a gravel pack screen assembly in place with the hydraulic fracturing treatment being pumped through the annular space between the casing and screen. In this situation the hydraulic fracturing treatment ends in a screen out condition creating an annular gravel pack between the screen and casing. This allows both the hydraulic fracturing treatment and gravel pack to be placed in a single operation. In other cases the fracturing treatment may be performed prior to installing the screen and placing a gravel pack.

[006] Fracturing fluids, gravel packing carrier fluids and frac pack fluids generally must be highly viscous to be able to suspend particulates. To achieve a high viscosity, viscosifiers often are added to such fluids. Such viscosifiers are expensive. Moreover, as a fracture or a

gravel pack is created a portion of the liquid contained in the fluid may leak off into the formation and/or may create an undesirable filter cake comprising deposited viscosifier on the walls of the fracture, well bore, or the formation.

[007] Filter cakes are sometimes desirable to aid in preventing drilling and other servicing fluids from being lost in the formation and to prevent solids from entering the porosities of the producing formation. However, just as a filter cake may block the loss of fluids into the formation, the same filter cake may block the production of fluids from the formation. Thus, the presence of a filter cake on a producing zone is generally undesirable when a subterranean formation is returned to production. Moreover, residue of viscosifiers used in subterranean applications often remains on the particulates transported in the viscosified fluid and may reduce the conductivity of packs made from such particulates.

[008] Also, as more wells are being drilled in deep water and in high temperature zones, gravel packing in long open horizontal well bores is becoming more prevalent. Completion operations in these wells generally involve the use of reduced-specific gravity particulates that are resistant to degradation in the presence of hostile conditions such as high temperatures and subterranean treatment chemicals. In order to prevent damage to these producing zones by gravel packing operations, the treating fluid carrying the particles should generally exhibit a relatively low viscosity. Similarly, fracture stimulation treatments carried out in deep, high temperature wells require similar reduced-specific gravity, spherical particles in lower viscosity fluids.

[009] Traditional high-strength particulates used in subterranean applications often exhibit too high of a specific gravity to be suspended in such lower viscosity fluids. While low specific gravity particulates, such as walnut hulls are well known in the art, generally they are not able to withstand significant closure stresses over time at elevated subterranean temperatures. Similarly, a variety of light-weight particles formed of thermoplastic materials including polyolefins, polystyrene divinylbenzene, polyfluorocarbons, polyethers etherketones and polyamide imides are commercially available. However, when these particles are exposed to temperatures above about 150°F, they soften and deform, and are not suitable in all well bores.

## SUMMARY OF THE INVENTION

[010] The present invention relates to improved particulates and methods of using such particulates in subterranean applications. More particularly, the present invention relates to reduced specific gravity particulates and their use in subterranean applications such as production enhancement and completion.

[011] One embodiment of the present invention provides particulates comprising silica and an aluminum oxide, at least one void, and have a specific gravity of less than about 2.2, a particle size of 8 U.S. mesh or smaller, and a substantially spherical shape.

[012] Another embodiment of the present invention provides particulates comprising at least about 30% silica, less than about 25% aluminum oxides, and a plurality of internal voids.

[013] Still another embodiment of the present invention provides a method of fracturing a subterranean formation comprising the steps of: providing a first fluid; providing a second fluid comprising particulates wherein the particulates comprise silica and an aluminum oxide, at least one void, and have a specific gravity of less than about 2.2, a particle size of 8 U.S. mesh or smaller, and a substantially spherical shape; placing a first fluid into the subterranean formation at a pressure sufficient to create or enhance at least one fracture therein; placing a second fluid into the subterranean formation and fracture; reducing the viscosity of the first fluid; reducing the viscosity of the second fluid so as to deposit the particulates into the fracture; substantially removing the first fluid and second fluid from the fracture while leaving at least a portion of the particulates in the fracture. The first fluid may be the same as or different than the second fluid.

[014] Other and further objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments which follows.

## DESCRIPTION OF PREFERRED EMBODIMENTS

[015] The present invention relates to improved particulates and methods of using such particulates in subterranean applications. More particularly, the present invention relates to reduced specific gravity particulates and their use in subterranean applications such as production enhancement and completion.

[016] The reduced-specific gravity particulates of the present invention comprise combustion products of carbonaceous materials such as oil, wood, garbage, sewage, hydrocarbons, coal, and the like. Typically, such combustion products suitable for use in the present invention comprise from about 30 to about 70 percent by weight silica and from about 5 to about 25 percent by weight aluminum oxides, with the majority of the balance being oxides of calcium, magnesium, potassium, sodium, iron, and titanium. Generally, the combustion products also comprise materials that will form gas when exposed to sintering temperatures.

[017] In some embodiments of the present invention, the combustion products may comprise "fly ash." Fly ash, as referred to herein, refers to a finely divided residue resulting from the combustion of carbonaceous material, such as ground or powdered coal, and generally carried by generated flue gases. One preferred fly ash is ASTM class F fly ash, having a Blaine fineness of about 10,585 square centimeters per gram and commercially available from Halliburton Energy Services, Inc., of Houston, Texas, under the trade designation "POZMIX®." In other embodiments of the present invention, the combustion product may comprise "bottom ash." Bottom ash, as referred to herein, refers to a finely divided residue resulting from the combustion of carbonaceous material and generally accumulating on the floor of an incinerator.

[018] The particulates of the present invention have low specific gravities, preferably below about 2.2. To create particulates having a suitably low specific gravity, it is desirable to control the respective percentages of metal oxides in the final particulate. For example, Table 1 below shows the pure compound specific gravities for a variety of common oxides:

**Table 1: Specific Gravity of Metal Oxides**

$\text{Fe}_2\text{O}_3$	5.2
$\text{TiO}_2$	4.2
$\text{Al}_2\text{O}_3$	4.0
$\text{MgO}$	3.6
$\text{CaO}$	3.3
$\text{Al}_2\text{O}_3\cdot\text{SiO}_2$	3.2
$\text{CaO}\cdot\text{Al}_2\text{O}_3$	3.0
$\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$	2.8
$\text{CaO}\cdot\text{SiO}_2$	2.5
$\text{SiO}_2$	2.3

[019] As shown in Table 1, aluminum oxides, such as  $\text{Al}_2\text{O}_3$ , are relatively heavy and, as such, the relative degree that these are present in the particulates of the present invention should be considered in light of the desired specific gravity of the particulates. The prior art, however, teaches that aluminum oxides are necessary to impart sufficient crush-resistance to a particulate so that it is useful in subterranean applications. Nevertheless, it has been determined that suitable crush-resistance may be obtained even while the concentration of aluminum oxides in the particulates is greatly reduced. In fact, in some embodiments of the present invention, the percentage by weight of aluminum oxides can be reduced to about 25%, about 10%, or even to zero and yet still produce a product with a crush strength suitable for use in most subterranean applications. By way of example, in one embodiment of the present invention, a particulate may comprise about 60% silica, about 20% alumina oxides, and about 5% calcium oxides.

[020] The particulates of the present invention generally exhibit crush strengths such that they can withstand pressures of at least about 1,000 psi without undesirable performance. One way to determine particulate crush strength is to place a known weight of particulates into a cylinder, apply a known pressure to the cylinder over a one minute time period, hold the pressure for two minutes, and then, once the pressure is released, to determine the weight of the fines produced by the pressure. If the weight of the fines is less than about 20% of the total weight of particulates placed in the cylinder then the particulates can be said to have withstood the pressure applied.

[021] In some preferred embodiments of the present invention, the particulates are capable of withstanding a pressure of at least about 2,500 psi. By way of example, a particulate comprising about 53% by weight  $\text{SiO}_2$  and about 26% by weight  $\text{Al}_2\text{O}_3$  has been shown to withstand pressures of about 5,000 psi without substantially degrading.

[022] The particulates of the present invention may be made by a process comprising pelletizing and sintering the compositions of the present invention. One embodiment comprises forming a composition comprising combustion products and a binder; pelletizing the mixture into discrete particulates; and sintering the discrete particulates at temperatures above about 1000°C to produce reduced-density particulates. Optionally, the discrete particulates may be dried or roasted at temperature between about 65°C to about 150°C prior to sintering the particulates. Such drying acts, *inter alia*, to reduce the particulate's water content.

[023] Binders used in sintering, such as clay, are well known in the art and it is within the ability of one skilled in the art to choose a binder for use in the sintering step of the methods of the present invention. Also known in the art is the fact that a fluid, such as water, is commonly used with the binder in a pelletizing process.

[024] By way of example, in some embodiments of the present invention, the combustion products comprise from about 50% to about 80% by weight of the mixture to be pelletized and the binder comprises from about 0.1% to about 5% by weight of the mixture to be pelletized. Where a fluid such as water is used along with the binder in a pelletizing process, the fluid may comprise from about 10% to about 25% by weight of the mixture to be pelletized.

[025] When such combustion products are pelletized and sintered, they produce particulates that are substantially spherical and that exhibit specific gravities of below about 2.2. The term "spherical" is used in this invention will designate pellets having an average ratio of minimum diameter to maximum diameter of about 0.7 or greater. The size of the particulates of the present invention is generally about 8 U.S. mesh or smaller. Having such a particle size allows the particulates to be useful in sand control operations such as gravel packing and production enhancing operations such as fracturing. One skilled in the art with the benefit of this disclosure will recognize the appropriate size for a given application.

[026] Processes capable of producing spherical pellets are well known in the art. One such method that may be used to produce the particulates of the present invention involves placing combustion products, binder, and a fluid such as water into a high intensity mixer. One

such suitable high intensity mixer is the RV02 High Intensity Mixer available from Eirich Machines, Inc. of Gurnee, Illinois. As the mixture exits the high intensity mixer, it may then be poured onto a slanted, rotating table. The size of the particulate may be influenced, *inter alia*, by affecting the speed of the table's rotation and the angle of the table's slant.

[027] The specific gravity and crush strength of the particulates of the present invention may be influenced, in part, by adjusting, *inter alia*, the percentage of materials in the combustion products that will form gas when sintered; the residence time; the rate of heating in the sintering process; and, the final sintering temperature. For example, as the percentage of materials in the combustion products that will form gas when heated increases, the porosity of the sintered particulate will increase, thus decreasing the particulate's specific gravity and crush-resistance. Moreover, as the residence time in the sintering process and the final sintering temperature increase, the specific gravity of the particulate may increase as porosities within the particulate decrease.

[028] As the percentage of voids in the particulate increases, its specific gravity will decrease and its crush strength will decrease. By controlling the level of voids in the particulate it is possible to tailor a proppant for the specific gravity and crush strength needed in a particular application. When the particulate is sintered, the materials in the combustion products that will form gas when heated leave behind voids and pore spaces in the particulate. Thus, it follows that the level of materials in the combustion products that will form gas when sintered in the pelletized particulate prior to sintering is related to the final level of porosity of the particulate. Thus, as the rate of heating in the sintering process increases, the specific gravity of the particulate may decrease as more porosities are created by the rapid formation of gas in the particulate.

[029] The particulates of the present invention may be heated by any means known in the art. The heating may be batch or continuous. In one continuous heating method, a rotary kiln may be used. A rotary kiln may be a refractory lined cylinder that is fired either directly or indirectly. In a directly fired rotary kiln, heat is provided at one end of the rotating cylinder and the feed of particulates to be heated is provided at the opposite end. Manipulatable kiln parameters include the revolution rate of the cylinder, the tilt angle of the cylinder, the final kiln temperature, and the temperature gradient along the cylinder. One skilled in the art with the

benefit of this disclosure will be able to determine the kiln parameters needed to produce a desired particulate.

[030] If a higher porosity particulate is desired, the particulate may be flash-roasted prior to sintering. Flash roasting acts, *inter alia*, to rapidly drive gases and residual water from the pelletized particulate and to create fissures within the particulate. Flash roasting herein refers to rapidly heating the particulates. If the heating occurs at a high enough rate, the materials that will form gas when heated will quickly exit the particulate. Such a rapid exit yields a porous structure wherein the at least some pores communicate with the exterior. Such pores may be thought of as "intercommunicating pores" because they connect a point inside the particulate with the particulate's surface and the environment surrounding the particulate. Flash roasting may be performed in a standard fluidized bed reactor. Generally, in such a reactor heated gases are fed from below a charge of particulates such that the particulates are lifted and mixed at a high rate while being heated. One flash roaster suitable for use in the present invention is a Torbed ® reactor commercially available from Torftech Limited, Ferndale Court, West End Road Mortimer, Reading RG7 3SY, Berkshire, United Kingdom.

[031] Another method of increasing the final level of porosity of the particulate is to include a clay material in the feed mixture of combustion products. Clays inherently contain water molecules that will release when the particulate is flash-roasted or sintered.

[032] Particulates having intercommunicating pores may be used to deliver treatment chemicals to a subterranean formation. A treatment chemical may be introduced into the pores of the particulate and then the particulate may be delivered to the subterranean formation. The treatment chemical may then exit the pores via diffusion. Chemicals suitable for delivery on porous media include but are not limited to gel breakers, oxidizers, enzymes, hydrolyzable esters, scale inhibitors, biocides, corrosion inhibitors, paraffin inhibitors, and substantially any other chemical that is soluble in the formation fluids under the environmental conditions of the formation within which it is placed. The particulates of the present invention may be impregnated with any of the above chemicals by any means known in the art.

[033] In some embodiments of the present invention, at least one of the voids created in the particulate is an internal void. That is, the void is entirely enclosed inside the particulate and does not communicate with the particulate's surface. Where it is desirable to minimize intercommunicating pores and create, instead, internal voids, one method of forming such voids



is to expose the particulate to higher sintering temperatures for a brief period of time such that the external surface of the particle vitrifies, thus forming a skin on at least a portion of the outer layer of the particulate such that voids communicating with the particulates may be sealed off.

[034] Many subterranean treatments require that particulates be suspended in a treatment fluid and carried into the subterranean formation. Generally, the treatment fluid must exhibit a viscosity high enough to suspend the particulates. The reduced specific gravity of the particulates of the present invention allows for the use of lower viscosity servicing fluids. In one embodiment of the present invention, a treatment fluid comprising a hydrocarbon or water carrier fluid comprising reduced-specific gravity particulates of the present invention suspended therein is pumped into a subterranean formation and at least a portion of the particulates are deposited therein.

[035] One embodiment of a method of the present invention provides an improved method of treating a subterranean formation using a treatment fluid comprising a hydrocarbon or water carrier fluid and reduced-specific gravity particles of the present invention suspended therein. In the treatment methods of the present invention, a treatment fluid comprising a hydrocarbon or water carrier fluid comprising reduced-specific gravity particles of the present invention suspended therein is placed into a subterranean formation and then the carrier fluid's viscosity is reduced so as to deposit at least a portion of the reduced-specific gravity particles in a desired location in the subterranean formation.

[036] Still another method of the present invention provides an improved method of hydraulic fracturing using reduced specific gravity particulates of the present invention. In some hydraulic fracturing methods of present invention, a first fluid is placed in the subterranean formation at a rate and pressure sufficient to form at least one fracture in the subterranean formation. Next, a second fluid comprising particulates of the present invention is placed into the fractures. Next, the viscosity of the first fluid is reduced, *inter alia*, to facilitate its removal from the subterranean formation and the viscosity of the second fluid is reduced, *inter alia*, to deposit the suspended particulates in the fracture and, *inter alia*, to facilitate the removal of the second fluid from the subterranean formation. Finally, the reduced viscosity first fluid and second fluid are substantially removed from the fracture and the subterranean formation.

[037] Another method of the present invention provides an improved method of gravel packing a delivery fluid comprising a hydrocarbon or water carrier fluid comprising reduced-

specific gravity particles of the present invention suspended therein. In some of the gravel packing methods of the present invention, a gravel pack composition comprising a carrier fluid having reduced-specific gravity particles of the present invention suspended therein is placed in a region of a well bore such that at least a portion of the gravel particles form a gravel pack substantially adjacent to the well bore. Then the viscosity of the delivery fluid remaining in the well bore may be reduced so that it may then be removed from the subterranean formation.

[038] Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit and scope of this invention as defined by the appended claims.

What is claimed is:

1. Particulates comprising silica and an aluminum oxide and at least one void and having a specific gravity of less than about 2.2, a particle size of 8 U.S. Mesh or smaller, and a substantially spherical shape.
2. The particulates of claim 1 comprising from about 30 percent to about 70 percent by weight silica.
3. The particulates of claim 1 comprising from about 0.1 percent to about 25 percent by weight aluminum oxides.
4. The particulates of claim 1 further comprising calcium oxides.
5. The particulates of claim 1 wherein the silica and aluminum oxides comprise combustion products of carbonaceous materials.
6. The particulates of claim 1 comprising a particle size of 25 U.S. mesh or smaller.
7. The particulates of claim 1 wherein the particulate is capable of withstanding a closure stress of at least about 2,500 psi.
8. The particulates of claim 1 comprising a vitrified outer layer.
9. The particulates of claim 1 wherein at least one void communicates between an interior of the particulate, and a surface of the particulate and environment surrounding the particulate.

10. Particulates comprising at least about 30% silica, less than about 25% aluminum oxides, and a plurality of internal voids.
11. The particulates of claim 10 comprising at least about 40 percent by weight silica.
12. The particulates of claim 10 comprising less than about 20% by weight aluminum oxides.
13. The particulates of claim 10 further comprising calcium oxides.
14. The particulates of claim 10 wherein the silica and aluminum oxides comprise combustion products of carbonaceous materials.
15. The particulates of claim 10 comprising a particle size of 25 U.S. mesh or smaller.
16. The particulates of claim 10 wherein the particulate is capable of withstanding a closure stress of at least about 2,500 psi.
17. The particulates of claim 10 comprising a vitrified outer layer.

18. A method of making a low-specific gravity particulate comprising the steps of:
- (a) providing combustion products of carbonaceous materials comprising silica and an aluminum oxide,
  - (b) mixing the combustion products with a binder to create a pelletizable mixture;
  - (c) pelletizing the combustion products of carbonaceous materials to create a pellet, and
  - (d) sintering the combustion products of carbonaceous materials to create a particulate comprising silica and an aluminum oxide and at least one void and having a specific gravity of less than about 2.2, a particle size of 8 U.S. Mesh or smaller, and a substantially spherical shape.
19. The method of claim 18 wherein the particulate comprises from about 30 percent to about 70 percent by weight silica.
20. The method of claim 18 wherein the particulate comprises from about 0.1 percent to about 25 percent by weight aluminum oxides.
21. The method of claim 18 wherein the particulate further comprises calcium oxides.
22. The method of claim 18 wherein the particulate further comprises a particle size of 25 U.S. mesh or smaller.
23. The method of claim 18 wherein the particulate is capable of withstanding a closure stress of at least about 2,500 psi.
24. The method of claim 18 wherein the sintering step occurs at a temperature above about 1000°C.
25. The method of claim 18 further comprising, between steps (c) and (d), the step of: drying the pellet at a temperature between about 65°C to about 150°C.
26. The method of claim 18 further comprising, between steps (c) and (d), the step of: roasting the pellet at a temperature of above about 200°C.
27. The particulates of claim 18 comprising a vitrified outer layer.
28. The particulates of claim 18 wherein at least one void communicates between an interior of the particulate, and a surface of the particulate and environment surrounding the particulate.

29. A method of fracturing a subterranean formation comprising the steps of:  
providing a first fluid;  
providing a second fluid comprising particulates wherein the particulates comprise silica and an aluminum oxide, at least one void, a specific gravity of less than about 2.2, a particle size of 8 U.S. Mesh or smaller, and a substantially spherical shape;  
placing a first fluid into the subterranean formation at a pressure sufficient to create at least one fracture therein;  
placing a second fluid into the subterranean formation and fracture;  
reducing the viscosity of the first fluid;  
reducing the viscosity of the second fluid so as to deposit the particulates into the fracture.
30. The method of claim 29 wherein the first fluid and the second fluid are the same fluid.
31. The method of claim 29 wherein the first fluid and the second fluid are not the same fluids.
32. The method of claim 31 wherein the viscosity of the first fluid is greater than the viscosity of the second fluid.
33. The method of claim 29 wherein the particulate comprises from about 30 to about 70 percent by weight silica.
34. The method of claim 29 wherein the particulate comprises from about 0.1 to about 25 percent by weight aluminum oxides.
35. The method of claim 29 wherein the particulate further comprises calcium oxides.
36. The method of claim 29 wherein the silica and aluminum oxides comprise combustion products of carbonaceous materials.
37. The method of claim 29 wherein the particulate comprises a particle size of 25 U.S. Mesh or smaller.
38. The method of claim 29 wherein the particulate is capable of withstanding a closure stress of at least about 2,500 psi.
39. The method of claim 29 wherein the particulate comprises a vitrified outer layer.

40. The method of claim 29 wherein at least one void of the particulate communicates between an interior of the particulate, and a surface of the particulate and environment surrounding the particulate.

41. A method of fracturing a subterranean formation comprising the step of:  
providing a first fluid;  
providing a second fluid that is different from the first fluid wherein the second fluid comprises particulates comprising silica and an aluminum oxide, a particle size of 8 U.S. Mesh or smaller, and a substantially spherical shape;  
placing a first fluid into the subterranean formation at a pressure sufficient to create at least one fracture therein;  
placing a second fluid into the subterranean formation and fracture;  
reducing the viscosity of the first fluid;  
reducing the viscosity of the second fluid so as to deposit the particulates into the fracture.
42. The method of claim 41 wherein the viscosity of the first fluid is greater than the viscosity of the second fluid.
43. The method of claim 41 wherein the particulate comprises from about 30 to about 70 percent by weight silica.
44. The method of claim 41 wherein the particulate comprises from about 0.1 to about 25 percent by weight aluminum oxides.
45. The method of claim 41 wherein the particulate further comprises calcium oxides.
46. The method of claim 41 wherein the silica and aluminum oxides comprise combustion products of carbonaceous materials.
47. The method of claim 41 wherein the particulate comprises a particle size of 25 U.S. Mesh or smaller.
48. The method of claim 41 wherein the particulate is capable of withstanding a closure stress of at least about 2,500 psi.
49. The method of claim 41 wherein the particulate comprises a vitrified outer layer.
50. The method of claim 41 wherein at least one void of the particulate communicates between an interior of the particulate, and a surface of the particulate and environment surrounding the particulate.



51. A method of installing a gravel pack in a well bore comprising the steps of:  
providing a gravel pack composition comprising particulate and a delivery fluid wherein the particulates comprise silica and an aluminum oxide, at least one void, a specific gravity of less than about 2.2, a particle size of 8 U.S. Mesh or smaller, and a substantially spherical shape;

introducing the gravel pack composition to the well bore such that the particulates form a gravel pack substantially adjacent to the well bore.

52. The method of claim 51 wherein the particulate comprises from about 30 to about 70 percent by weight silica.

53. The method of claim 51 wherein the particulate comprises from about 0.1 to about 25 percent by weight aluminum oxides.

54. The method of claim 51 wherein the particulate further comprises calcium oxides.

55. The method of claim 51 wherein the silica and aluminum oxides comprise combustion products of carbonaceous materials.

56. The method of claim 51 wherein the particulate comprises a particle size of 25 U.S. Mesh or smaller.

57. The method of claim 51 wherein the particulate is capable of withstanding a closure stress of at least about 2,500 psi.

58. The method of claim 51 wherein the particulate comprises a vitrified outer layer.

59. The method of claim 51 wherein at least one void of the particulate communicates between an interior of the particulate, and a surface of the particulate and environment surrounding the particulate.

**IMPROVED PARTICULATES FOR SUBTERRANEAN APPLICATIONS AND  
METHODS OF UTILIZING THESE PARTICULATES IN  
SUBTERRANEAN APPLICATIONS**

**Abstract of the Disclosure**

[039] The present invention involves reduced specific gravity particulates and their use in subterranean applications such as production enhancement and completion. One embodiment of the present invention provides particulates comprising silica and an aluminum oxide and at least one void and having a specific gravity of less than about 2.2, a particle size of 8 U.S. Mesh or smaller, and a substantially spherical shape. Other embodiments of the present invention provide for using such particulates in subterranean operations such as fracturing and gravel packing.

**APPENDIX E: U.S. PATENT NO. 6,913,643 (“DEJAIFFE”)**



US006913643B2

(12) **United States Patent**  
**Dejaiffe**(10) **Patent No.: US 6,913,643 B2**(45) **Date of Patent: Jul. 5, 2005**(54) **LIGHTWEIGHT FOAMED GLASS  
AGGREGATE**(75) **Inventor: Robert Dejaiffe, Kennewick, WA (US)**(73) **Assignee: Integrated Environmental  
Technologies, LLC, Richland, WA (US)**(\*) **Notice:** Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 52 days.(21) **Appl. No.: 10/369,784**(22) **Filed: Feb. 18, 2003**(65) **Prior Publication Data**

US 2004/0162210 A1 Aug. 19, 2004

(51) **Int. Cl.<sup>7</sup> ..... C04B 14/24**(52) **U.S. Cl. .... 106/716**(58) **Field of Search ..... 106/716**(56) **References Cited****U.S. PATENT DOCUMENTS**4,347,326 A \* 8/1982 Iwami et al. .... 501/39  
6,616,752 B1 \* 9/2003 Basura et al. .... 106/716  
6,642,164 B2 \* 11/2003 Akaishi ..... 501/80**FOREIGN PATENT DOCUMENTS**BE 698871 \* 11/1967  
CH 690680 \* 12/2000  
DE 54626 \* 3/1967  
DE 59035 \* 12/1967  
DE 2409328 \* 8/1974  
DE 19603014 \* 7/1997  
DE 19910268 \* 9/2000  
DE 2000 6615 \* 9/2000  
DE 10031899 \* 3/2001  
DE 10159340 \* 6/2002  
EP 665195 \* 8/1995  
EP 999193 \* 5/2000  
EP 1085138 \* 3/2001  
HU 15032 \* 6/1978  
HU 40056 \* 11/1986HU 66618 \* 12/1994  
JP 59088363 \* 5/1984  
JP 59203755 \* 11/1984  
JP 60204646 \* 10/1985  
JP 08081251 \* 3/1996  
JP 09124378 \* 5/1997  
JP 11199346 \* 7/1999  
JP 11278900 \* 10/1999  
JP 2000026136 \* 1/2000  
JP 2000247764 \* 9/2000  
JP 2001106552 \* 4/2001  
JP 2002070028 \* 3/2002  
SU 135 7388 \* 12/1987  
WO WO 9502562 \* 1/1995  
WO WO 9817452 \* 4/1998  
WO WO 2001020094 \* 3/2001**OTHER PUBLICATIONS**Practical study on super lightweight cellular concrete—the  
influence of lightweight aggregates & cellular form on early  
age shrinkage of concrete, Semento, Konkurito Ronbunshu  
(2000), 54, 680–86.\*“Heat insulating properties of enclosing structures based on  
foamed glass granulate”, Saakyan, Stroitel 'nye Materialy  
(1991), 6, 3–4.\*“Lightweight concretes from foamed glass granules” Put-  
lyayev et al., Beton i Zhelezobeton (Moscow, Russ. Fed) 11,  
15–16, 1990.\*

\* cited by examiner

*Primary Examiner*—Paul Marcantoni(74) *Attorney, Agent, or Firm*—Douglas E. McKinley, Jr.(57) **ABSTRACT**A lightweight aggregate for use in concrete exhibiting a high  
weight to strength ratio comprising a mixture of hydrated  
cement and a low sodium closed-cell foamed glass com-  
prised of between 51 and 65 weight percent silica, between  
8 and 14 weight percent alumina, between 2 and 5 weight  
percent soda, between 18 and 26 weight percent calcia,  
between 2 and 5 weight percent iron oxide, and up to 8  
percent lithium oxide.**7 Claims, No Drawings**

# LIGHTWEIGHT FOAMED GLASS AGGREGATE

## CROSS-REFERENCE TO RELATED APPLICATIONS

Not Applicable

## BACKGROUND OF THE INVENTION

The cost and energy associated with the production and/or mining of raw materials for use in consumer and industrial products, together with the cost, energy, and environmental consequences of disposal the byproducts formed during fabrication of finished products, and the disposal of finished products themselves post-use, creates enormous incentives towards finding secondary uses for unwanted materials. Enormous investments in recycling and waste to energy technologies over the past several decades are testament to the economic advantages inherent in re-using and recycling materials. Competitive pressures, combined with these economic advantages, have resulted in the adaptation of waste minimization technologies, recycling, and re-use programs by virtually all major manufacturing industries. However, despite the economic advantages created by these strategies, massive volumes of the byproducts of industrial production and finished products post-use are still typically in a condition unsuitable for re-use and recycling, and huge volumes of these materials are disposed of in landfills and hazardous waste disposal sites on a daily basis.

Some of the more vexing difficulties that prevents more widespread adaptation of re-use and recycling strategies are related to the inherent hazardous nature of many of these materials, the cost and expense of processing heterogeneous streams of these waste materials, and finding applications for re-use that would consume significant volumes of these materials. One application for re-use that has long been recognized as having the potential for high volume usage is as a construction material. For example, concrete is exceeded only by water in the commercial tonnage used annually in the United States. Thus, any product or bi-product that could conceivably be utilized as an aggregate in a concrete mixture would have an enormous "sink" through which the materials could be re-used and thereby incorporated into valuable products. These advantages have led to the incorporation of fly ash generated in commercial boilers and blast furnace slag into concrete for construction. Some of the advantages of using fly ash in concrete were set forth in the Naval Facilities Engineering Service Center (NFESC) Technical Report TR-2195-SHR "Alkali-Silica Reaction Mitigation State-Of-The-Art" by L. J. Malvar, published in October 2001, the entire contents of which are incorporated herein by this reference. As described in the NFESC report, the use of Class F (low calcium) fly ash as a replacement for Portland cement in amounts around 25% has been shown to mitigate the effects of the Alkali-Silica Reaction (ASR) in concrete. Briefly, the ASR takes place when silica is surrounded by high pH cement paste, typically as a result of the high calcium and other alkaline content of the cement. The silica in this environment tends to react with the calcium to form a gel of calcium silicate which tends to swell over a period of time, typically ranging from as little as a few months to a few years. This swelling causes stress in the concrete, thereby weakening it. As further pointed out in the NFESC report, the 25% Class F fly ash replacement also resulted in less expansion than 35% Class C fly ash, which the authors note had previously been shown to either

not reduce, or to aggravate the ASR problem. This is because the Class C fly ash exhibits a larger percentage of calcium. Thus, among the drawbacks associated with the widespread re-use of fly ash as an additive to concrete are differences associated with the differing types of fly ash, and their effect on the ASR in the final product.

Problems associated with the use of waste materials in concrete and ASR have also received notable attention with respect to glass materials. In U.S. Pat. No. 6,500,254, entitled "Cements including lithium glass compositions" issued Dec. 30, 2002 to Baxter et al., the entire contents of which are hereby incorporated herein by this reference, the inventors describe the use of lithium glass as an additive to concrete, and the minimization of ASR thereby. As described by the '254 patent, the lithium glass includes a glass forming oxide; lithium oxide; and optionally a glass network modifying oxide. The inventors further point out that the lithium glass can be essentially free of sodium or potassium ions. While the '254 patent does provide a means by which glass can be manufactured to be a useful additive to concrete, the use of the technology still has many practical drawbacks. For example, among the problems associated with the use of lithium glass as an additive to concrete is the energy intensive process through which glass is manufactured. As described by the inventors of the '254 patent, and as is also common in any commercial glass making operation, to form a glass requires the materials to be heated to a temperature sufficient to melt the glass, thereby allowing its formation. The high energy requirements for this melting operation often will dominate the economic benefits afforded by using glass as an additive. Further, the specific gravity of the resultant glass is similar to that of normal gravel aggregate. Thus, the resulting concrete produces similar or worse weight to strength ratios found in more traditional concrete mixtures.

Improved strength to weight ratios are the subject of wide interest in the concrete industry, and the search for suitable materials has attracted significant research and development investments. For example, Columbia-University has reported that "lightweight concrete is of utmost importance to the construction industry. Most of current research focuses on high-performance concrete by which is meant a cost-effective material that satisfies demanding performance requirements, including durability. The advantages of lightweight concrete are its reduced mass and improved thermal and sound insulation properties, while maintaining adequate strength. The reduced weight has numerous advantages, not the least of them being a reduced demand on energy during construction." The concrete materials research group at Columbia University further reports that they have developed a "new kind of lightweight concrete, which combines the advantages of normal-weight aggregate with cellular concrete, that is, good strength and durability properties as well as thermal and sound insulation." As described by the Columbia researchers, the key is "an admixture that introduces air bubbles into the cement matrix using normal mixing procedures and therefore can be combined with both normal and lightweight aggregate." Thus, while the group at Columbia has apparently discovered a method for producing lightweight concrete, they have not addressed the need for the discovery of lightweight aggregates that incorporate byproducts or waste products in an economically advantageous way, or which would incorporate those materials in a manner which would prevent ASR.

Traditional approaches for large sized lightweight aggregate have included the use of materials such as perlite, expanded shale, and other naturally occurring porous rocks.

Recently, research has examined sintered materials for use as a lightweight aggregate. Typically under either of these approaches, the material has an open structure, allowing it to absorb water. This can complicate the concrete forming process as the aggregate will often compete with the cement for available water. Thus, the aggregate is either soaked in water prior to mixing, which can lead to excess water and less than optimal curing, or the aggregate is mixed with the cement immediately prior to use, thus necessitating the additional cost and inconvenience of mixing at or near a jobsite. Further, few small-sized lightweight aggregates have been developed. The industry still relies mainly on sand for small sized aggregates, which, while providing excellent flowability in the concrete mix prior to curing does not provide a particularly advantageous strength to weight ratio in the final product.

Therefore, there exists a need for methods and materials whereby byproducts or waste products can be incorporated into concrete mixtures in an economically advantageous way, which does not result in an unacceptable ASR. There further exists a need for methods and materials that will produce aggregate for concrete in a lightweight form, thereby allowing the formation of a final concrete product having a favorable strength to weight ratio. Most preferably, there exists a need for methods and materials that allow both the incorporation of industrial byproducts and waste products into concrete mixtures in an economically advantageous way in a lightweight form, thereby allowing the formation of a final concrete product having a favorable strength to weight ratio, and which does not result in an unacceptable ASR in the final concrete product. There also exists a need for lightweight aggregate materials that do not absorb water and which can be provided as having small particle sizes to allow a replacement for sand.

#### SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method for forming a lightweight aggregate suitable for use as an aggregate in concrete. More particularly, it is an object of the present invention to provide a glass material suitable for use as a lightweight aggregate in concrete. It is a further object of the present invention to provide a glass material that is suitable for use as a lightweight aggregate in concrete which requires minimal processing beyond processing that is currently performed in existing industrial processes. It is a further object of the present invention to provide a glass material that is suitable for use as a lightweight aggregate in concrete which requires minimal processing beyond the processing that is currently performed in existing industrial processes and which incorporates a wide variety of waste materials which are otherwise currently disposed of in industrial landfills and/or hazardous waste disposal facilities. It is a further object of the present invention to provide a glass material suitable for use as a lightweight aggregate in concrete which requires minimal processing beyond the processing that is currently performed in existing industrial processes which incorporates a wide variety of waste materials and which minimizes ASR within the resultant cement product. It is a further object of the present invention to provide a glass material suitable for use as a lightweight aggregate in concrete that does not absorb water and/or which may be fabricated as having a small particle size, thereby allowing its use as a replacement to larger porous rocks and sand.

These and other objects of the present invention are accomplished through the use of glass materials formed in high temperature waste treatment systems using either plasma heating, joule heating, or combinations thereof, wherein said glasses are formulated as having a chemical

structure suitable for incorporation in cement or concrete, and wherein the glass formed in the high temperature waste treatment systems are further processed with foaming agents to form close celled structures resistant to water absorption. Preferably, the glasses formed by the present invention comprise between 51 and 65 weight percent silica, between 8 and 14 weight percent alumina, between 2 and 5 weight percent sodium oxide, between 18 and 26 weight percent calcium, between 2 and 5 weight percent iron oxide, and up to 8 percent lithium oxide. A variety of factors inherent in this composition provide a stable glass that will not degrade in a concrete mixture, and which will not promote ASR. Since the maintenance of a low pH at the surface of the aggregate will tend to assist the prevention of ASR in the final concrete product, it is preferred that the lightweight aggregate comprise less than 5 weight percent sodium. As used herein, the term "low sodium" thus denotes a glass composition having a sodium oxide content of 5% or less. Similarly, the inclusion of alumina will tend to protect the glass product from degrading.

Several advantages flow from the use of existing high temperature waste processing systems to formulate the light weight glass materials of the present invention. In the first instance, these waste treatment systems are already in use for processing a variety of waste materials. Thus, the energy necessary to melt the glass in its initial formation is already being expended. Also, skilled operators of these systems have the flexibility to adjust the inputs to these systems to produce the desired chemical properties in the resultant glass output. Further, the preferred chemical structure as described herein, allows these systems to incorporate a variety of otherwise difficult, and expensive to dispose of, waste streams at minimal additional cost. For example, glasses containing lithium oxides can be formed using post-consumer lithium batteries and/or lithium bearing spodumene mine tailings as a feed stream. Currently, these batteries are disposed of as waste products, and, due to their reactive nature, present an environmental hazard for the operators of solid waste disposal sites. Incorporating these waste batteries into a useful product, according to the present invention, turns this negative feature into a positive feature. Other materials currently disposed of in industrial landfills and at hazardous waste disposal sites which can be successfully incorporated into suitable glasses for use as an aggregate include fly ash (both Class F and Class C); waste consumer glass used as containers and the like, including colored glasses, used foundry sand, and bottom ash from industrial furnaces.

A further advantage of the present invention is the ability to use intermediate forms of the glasses in a beneficial manner. For example, once the glasses of the present invention are formed in a high temperature waste treatment system, they can be utilized as a high quality abrasive material similar in performance to those described in U.S. Pat. No. 5,462,570 issued Oct. 31, 1995 to Balcar, et al. and entitled "Process for producing an environmentally acceptable abrasive product from hazardous wastes", the entire contents of which are hereby incorporated herein by this reference, prior to forming them into the closed cell structure.

The formation of the glasses into a closed cell structure may be accomplished by heating the glass with foaming agents in a conventional manner, as well as by the methods described in U.S. patent application Ser. No. 09/777,802, filed Feb. 5, 2001, entitled "Crushed Glass Filter Aid and Method of Use" and U.S. patent application Ser. No. 10/011,944, filed Nov. 5, 2001, entitled "Foam Glass and Method of Making" the entire contents of each of which are hereby incorporated herein by this reference. Preferably, the lightweight aggregate of the present invention can be formed in

5

large and small sizes. For both sizes, a typical process begins by ball milling glass of a suitable composition. The glass is then mixed with a foaming agent, as needed. In the case of spray drying, the addition of a foaming agent may be unnecessary as the inherent moisture in the ball milled glass may be sufficient to result in acceptable foaming upon heating.

To form smaller sized lightweight aggregate, which is aggregate having a closed cell structure and approximately the size of sand, the glass is either pelletized, or spray dried, followed by firing in open flame in a manner similar to perlite expansion. Small sized lightweight aggregate provides numerous advantages. The small sized lightweight aggregate tends to distribute itself uniformly in a cementations mixture, thereby avoiding strength problems associated with localized concentrations of aggregate materials in the mixture. Notably, the use of the lightweight aggregates of the present invention are particularly compatible with aerated cement. Further, problems associated with ASR are less of a concern, as any swelling is evenly distributed, avoiding localized stresses that can lead to concrete failure.

Large lightweight aggregates having a closed surface may be formed by foaming the glass in an open ended mold. The size and shape of the light weight aggregates formed in this manner can be easily controlled, by controlling the size and shape of the molds, as well as the amount of starting materials. Close celled lightweight aggregates with open structure at the surface consisting of broken cells can be formed by crushing the large lightweight aggregates. Alternatively, close celled lightweight aggregates with open structure at the surface consisting of broken cells may be formed by spreading the glass and foaming agent on a sheet, heating the mixture, and breaking the resultant foam glass product up into desired aggregate sizes.

Under either approach, additional strength can be achieved by passing the lightweight aggregate through a flash firing process (such as exposure to an open flame) thereby forming a hardened shell. The resultant lightweight aggregate is thereby optimized to obtain the maximum strength to weight ratio.

As noted above, a further advantage of the present invention results from the capacity of the glasses to be used in industrial processes prior to foaming. For example, the glass compositions that are suitable for formation of lightweight aggregates are also suitable for use as a high quality abrasive material. In this manner, the materials find use in a series of industrial processes. First, they are used in the processes and products by which they are originally derived (eg. as the bi-product in the operation of industrial furnaces in the case of bottom ash and fly ash, and as consumer products in the case of colored glass beverage containers and lithium batteries). Then, after forming the materials into a glass, they are crushed and screened, and then used as high quality abrasive materials in industrial and commercial sand blasting operations. Finally, the used abrasive materials are foamed with a suitable blowing agent, where they are again used as a high quality, light weight aggregate in admixture with cement to form a lightweight concrete product. In this manner, a variety of industrial needs are met, while the cost and environmental consequences inherent in the extraction of raw materials is kept to a minimum.

Yet a further advantage of the present invention is derived from the need for additive materials in the operation of commercial high temperature waste treatment systems. In many applications, these high temperature waste treatment systems are utilized to treat waste streams having a high content of carbonaceous materials. For example, combination joule and plasma heated melters (such as the Plasma Enhanced Melter or PEM™ systems manufactured by the

6

assignee of the present invention) have found significant market acceptance processing medical wastes. These medical wastes tend to consist of high percentages of carbonaceous materials. The proper operation of the PEM™ systems thus can often require the introduction of materials necessary to provide a glass bath having the proper chemical characteristics necessary for proper operation of the PEM™ system. The present invention thus affords operators of these systems with the ability to use inputs that would otherwise require expensive and environmentally hazardous disposal, and produce a product that can be used in a series of industrial processes as outlined above.

In a preferred embodiment of the present invention, an admixture, typically called a pozzolan, is further added to the concrete formula to change, spread or reduce the silica reaction to prevent it from becoming a localized source of stress. As noted in the background section, Class F fly ashes have been shown to make good pozzolans, and the use of fly ash as an admixture is increasing in the concrete industry. In the present invention, a blend of fly ashes are used to make the glass aggregate material. This creates an apparent contradiction in that pozzolans (which deter ASR) can be used as the source of the oxides needed to make a glass (with a reputation for ASR problems.) The present invention overcomes this apparent dichotomy as the major difference between "bad" aggregate and "good" pozzolan is particle size (pozzolans are typically fine powders.) In addition, the present invention differs from ordinary waste glass, because the present invention contains alumina which reduces the silica content and increases chemical durability; the present invention contains less soda, reducing leachability; the present invention contains more calcia, promoting formation of cementitious products; and the present invention preferably contains iron, which is beneficial to the concrete.

## CLOSURE

While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

I claim:

1. A concrete material comprising a mixture of hydrated cement and a low sodium closed-cell foamed glass wherein the sodium oxide content of said glass is 5 weight percent or less.
2. The concrete material of claim 1 wherein said mixture additionally contains at least one pozzolan.
3. The concrete material of claim 1 wherein said hydrated cement is aerated.
4. The concrete material of claim 1 wherein said closed-cell foamed glass contains lithium oxide.
5. The concrete material of claim 1 wherein said closed-cell foamed glass has a hardened shell formed by a flash firing process.
6. The concrete material of claim 1 wherein said closed-cell foamed glass contains lithium oxide in an amount between about 0.1 to 8 weight percent.
7. A concrete material comprising a mixture of hydrated cement and a low sodium closed-cell foamed glass comprised of between 51 and 65 weight percent silica, between 8 and 14 weight percent alumina, between 2 and 5 weight percent sodium oxide, between 18 and 26 weight percent calcia, between 2 and 5 weight percent iron oxide, and up to 8 percent lithium oxide.

\* \* \* \* \*